Time Resolved Dynamics of Holes in p-type Germanium Photoexcited by Femtosecond Infrared Pulses

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We investigate the relaxation of a nonequilibrium distribution of holes generated in the spin-orbit split-off valence band in p-type germanium by femtosecond infrared pulse excitation. The redistribution and thermalization of the holes in the heavy-hole valence band is shown to occur in the first 550 femtoseconds after excitation. We follow the dynamics of the holes until their recombination with the ionized acceptors. Data with temperature ranging from 10 to 60 K reveal the recombination dynamics of the holes.

A study of carrier dynamics in semiconductors is of great value for understanding the fundamental scattering processes and transport in these materials. Early transport studies with large pulsed electric fields investigated the relaxation mechanisms in doped semiconductors[1-4]. A nonequilibrium distribution of carriers was induced by the applied electric field. Under these conditions, only a fraction of the carriers had an energy higher than an optical phonon. A more precise determination of the carrier relaxation times is possible with the improved time resolution offered by optical pulse excitation. These investigations can provide new insight in the interaction and cooling processes of hot carriers in semiconductors. The nonequilibrium distributions of carriers in bulk GaAs[5-9] and quantum well structures[10-13] were studied by optical spectroscopy with ultrashort laser pulses. In such experiments nonequilibrium distributions of electrons and holes created by interband excitation were studied on a very short time scale, but a separation of the electron and hole dynamics was difficult. In order to separatly investigate the relaxation of electron and hole distributions a doped semiconductor and infrared spectroscopy had to be used. The distribution of hot holes in p-type germanium was recently studied by performing optical excitation with infrared picosecond pulses[14]. These previous studies suggested that the relaxation of hot holes to a quasi equilibrium (hot Fermi) distribution occured on a subpicosecond time scale. However, inter- and intra- valence bands hole scattering times could not be determined because of limited time resolution.

In this paper, we report the direct time-resolved infrared femtosecond measurement of inter- and intra-valence band scattering of hot holes in p-type germanium. By measuring the absorption recovery, we follow the complete dynamics of holes from a nonequilibrium distribution generated in the spin-orbit split-off valence band until their recombination with the ionized acceptors. The change of absorption of the semiconductor is monitored with an unprecedented temporal resolution of 250 femtoseconds. The dynamics of the optically excited holes is also studied at several temperatures ranging from 10 to 60 K, which enables us to unravel the relaxation processes of the holes.

In our experiment we use a standard pump-probe technique: a first infrared pulse excites part of the holes from the acceptor levels to the spin-orbit split-off velence band. The resulting change of absorption is monitored as a function of the delay time between pump and probe pulses to deterrnine the relaxation dynamics. The sample is a gallium- doped germanium semiconductor with a thickness of 50 μm and a hole density

of 3×10^{17} cm^{-3}. The infrared pulses are generated by parametric frequency conversion[15]. Intense pulses at a wavelength of 620 nm are generated in a colliding-pulse mode- locked (CPM) dye laser and a six-pass dye amplifier that is pumped by a XeCl excimer laser (repetition rate up to 200 Hz) [16]. Part of the amplified pulses pumps a traveling- wave dye laser (TWDL). The output of the TWDL, which is recompressed by a pair of SF-10 prisms, and the second part of the amplified CPM pulses are focused onto a nonlinear LiIO3 crystal to generate the difference frequency in the infrared. The infrared pulse is generate at 3.16μm (390meV) having a band width and an energy per pulse of 20 meV and 10 nJ, respectively. The spectrum of the infrared pulse is plotted in Fig. 1c. A pulse duration of 250 femtoseconds is achieved with this scheme (Fig. 1b).

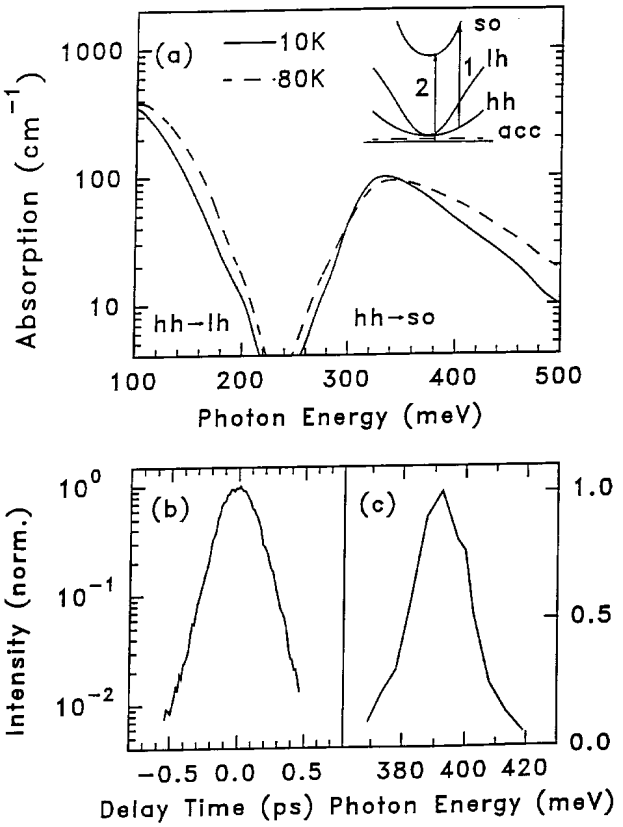

Figure 1. (a) Steady-state infrared absorption spectrum of p-type germanium (acceptor concentration: 3×10^{17} cm^{-3}) at lattice temperature of 10 K and 80 K. The absorption coeff1cient is plotted logaritmically vs photon energy. The electronic transitions relevant for our experiments are depicted in the inset. (b) Cross-correlation trace of the infrared pulses at 3.16 μm with 120 fs pulses from an amplified colliding-pulse mode-locked (CPM) dye laser. (c) Spectrum of the femtosecond infrared pulses.

In order to investigate the relaxation processes, we generate a nonequilibrium distribution of holes in the spin-orbit split-off (so) valence band. In p-type germanium semiconductor the optical transitions from the heavy-hole (hh) valence band and acceptor levels (build up mainly of heavy hole states) to the so-band are responsible for the observed absorption between 280 meV and 500 meV [14] (see Fig. 1a). At low temperatures, the infrared photon with an energy of 390 meV is absorved by the holes which are present in the acceptor levels and excite them to the so-band. At very low temperaures, T_L=10 K, the holes of the p-doped sample are bound to the acceptor atoms. In this case, infrared absorption invoves photoionization of shallow impurity states of an binding energy of 9 meV. In this temperature, the absorved photon with an energy of 390 meV promote mainly holes from the acceptor ground level to the so-band (inset in Fig. 1).

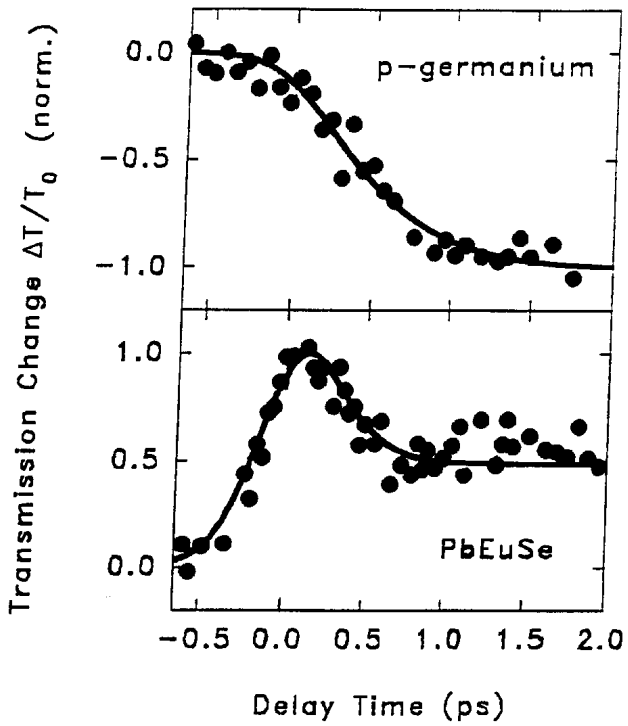

Figure 2. The transmission change $\Delta T = (T - T_0)/T_0$ of the sample plotted as a function of the delay time between pump and probe pulses (points; T, T_0: transmission with and without excitation of the sample); (a) induced absorption in p-germanium due to the transient change of the optically coupled states population, and (b) bleaching of the band gap absorption in PbEuSe semiconductor whose rise time gives the cross-correlation function of the pump and probe pulses.

In a first series of experiments we focus specifically on the fast relaxation dynamics of the holes within the first picosecond. In Fig. 2a we show the change of

transmission $\Delta T = (T - T_0)/T_0$ of the sample plotted as a function of the delay time between pump and probe pulses; T and T_0 are the transmission of the sample with and without excitation, respectivelly. We measure an increase of absorption of the sample without any initial bleaching of absorption. This indicates that the hole scatter from the initial states in the so-band in a time short compared to the pulse duration. We cannot then define the real zero time in the experiment. The zero delay time between the pump and probe pulses is determined independently by a pump and probe experiment in a PbEuSe semiconductor. In this case, we observe the usual bleaching of the sample absorption due to transition from valence to conduction band; consequently, the signal rises with the cross-correlation function of the pump and probe pulses (Fig. 2b). The absolute zero delay time from p-germanium absorption data is then known with an accuracy estimated to be about 10 percent.

In Fig. 3, we show the p-germanium data measured for temperatures ranging from 10 to 60 K. We measure an increase of absorption, with a rise time of 550 femtoseconds which does not change with temperature. At these low lattice temperatures the percentage of ionized holes is not significant to populate the states in the hh-band which are optically coupled to the so-band transitions (states which have the same wave vectors and are separeted by one photon energy). The holes are then generated in the so- band by making only transitions from acceptor levels. The changes of the hole distribution, a transient deplection of hh levels and an excess population of so states that are optically coupled by the femtosecond excitation pulse, are expected to cause a decrease of inter-valence-band absorption by state filling on an ultrafast time scale. However, this effect is clearly not observed in our data. This finding demonstrates that holes excited to so-band are scattered from their initial states in a time shorter than the pulse duration. These holes in the so-states are then scattered to the lh- and hh-bands with the emmission of an optical phonon via deformation potential generating a hot hole distribution in the hh-band. These hot heavy holes with an excess energy of around 350 meV and the unexcited holes present by doping occupying low-energy states around $\mathbf{k}$=0 represent a non-equilibrium distribution within the hh-band. Subsequently the high energy carriers loose their excess energy by transfering energy to the lattice via emission of optical phonons and the more important for thermalization, by heating the cold Fermi see (unexcited heavy holes) via inelastic hole-hole scattering. This thermalization form a hot quasi-equilibrium distribution characterized by an elevated hole temperature of $T_C = T_L + 50$ K. As a result, the holes populate the optically coupled states in the hh-band. The transient increase of the hole population in these states explains the observed increase of absorption in our experiment. Thus, this observed increase of absorption with rise time around 550 femtoseconds gives direct insight into the thermalization of the photoexcited holes. This interpretation is supported by theoretical calculations[17–20] where the rates of intervalence band scattering via the optical deformation potential were calculated in first-order perturbation theory taking into account the nonparablic valence-band structure and the k-dependent overlap of the corresponding hole wave functions[21,22]. The phonon scattering rates within the hh-band were calculated by the same formalism. Inelastic hole-hole scattering is treated in a model including the full dynamical screening of the Coulomb interaction as well as intra- and inter- valence-band transitions[19,20].

We investigate now subsequent dynamics of holes until their recombination with the ionized acceptors. Capture processes of holes were extensively studied by theoretical and experimental methods[23–26]. However, the role of the acceptor excited levels in the recombination process was, until now, only theoretically investigated by Monte Carlo simulations[25]. We show in Fig. 4, data measured on a long time scale at lattice temperatures from 10 to 60 K. The relaxation time constants of the measured signals are strongly affected by a temperature rise. We note that the initial distribution of holes depends substantially on the lattice temperature. At 10 K, before the excitation every acceptor is neutral and in its fundamental state (note that the acceptor ionization energy is equal to 10 meV). Consequently, the optically coupled states in the hh-band and in the excited levels of the acceptors are empty. Thus, the holes are mainly excited to the so-band by transitions from the acceptor ground state. At 40 K, the holes excited to the so-band are generated by transitions from the ground state of the acceptors as well as excited states because an amount of the acceptors are alread excited at this lattice temperature. At 60 K, the majority of holes are photo-excited from acceptor excited states to the so-band. Therefore, we can separatly investigate the recombination processes of holes with the acceptor excited states or ground state by measuring, at different

lattice temperatures, the time taken by holes to relax to their initial states. In Fig. 4a, we plot the data measured at 10 K. At this temperature we directly measure the holes relaxing to the acceptor ground state. The signal is a step function with a relaxation time constant of hundreds of picoseconds. When the temperature is rised to 40 K, the data can be fitted with two time constants (Fig. 4b): a decay relaxation time of 20 picoseconds followed by a step function lasting several hundreds of picoseconds. The fast time constante gives us the time taken by the holes to repopulate the excited states of the acceptors. The step function relaxation time represents the average time which the holes need to repopulate the acceptor ground state. The curve measured at 60 K is fitted with only one time constant: 10 picoseconds and does not exhibit any step function (Fig. 4c). the fast dynamics corresponds to a return to an equilibrium distribution, which is the same initial distribution of holes in the excited acceptor levels before excitation.

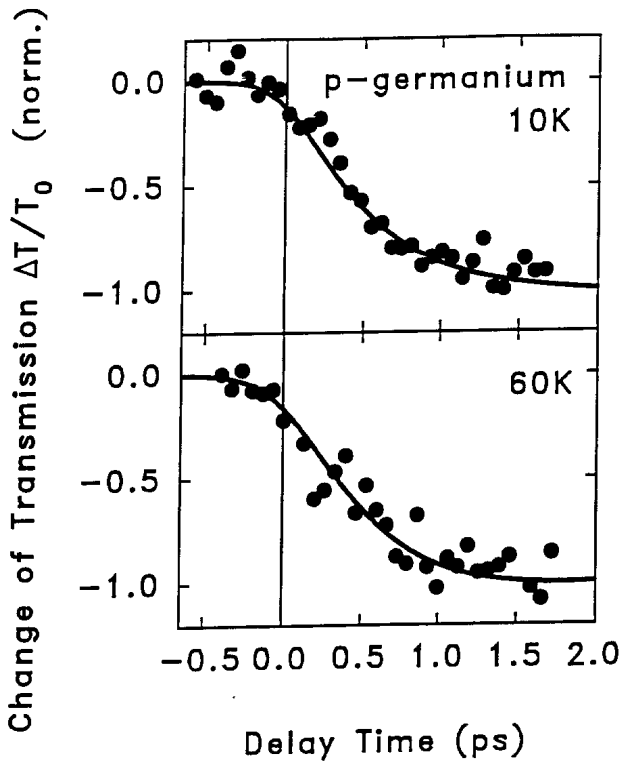

Figure 3. Short time evolution of the transmission in p-germanium measured at 3.16 μm (392 meV) for two different lattice temperatures: (a) 10 K and (b) 60 K. The normalized change of transmission $\Delta T = (T - T_0)/T_0$ is plotted for delays up 2.0 ps.

On describe the hole recombination process as follow: On a subpicosecond time scale, the holes are redistributed in the hh-band and reach a quasi-equilibrium

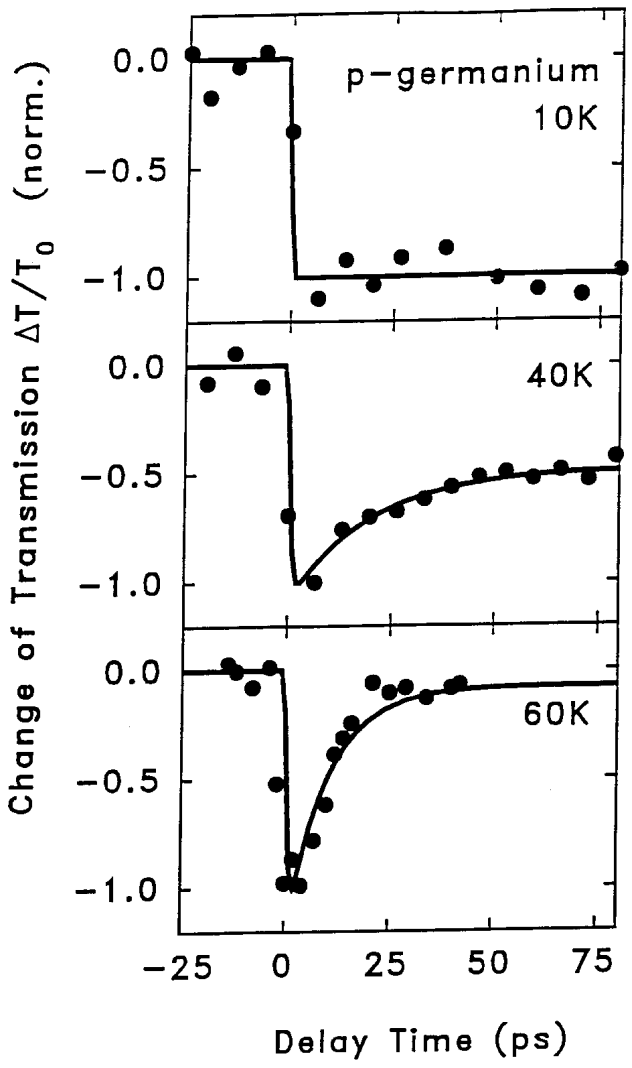

Figure 4. Long time scale evolution of the transmission in p-germanium. The time dependent induced absorption at different temperatures of the lattice, (a) 10 K, (b) 40 K and (c) 60 K, reveals the relaxation dynamics of the photoexcited holes.

distribution, as described above (see Fig. 3). Subsequent cooling of the holes proceeds essentially by emission of optical phonons via deformation potentia[14]. The holes loose their energy to the lattice until reaching an equilibrium distribution by populating the low energy states of the hh-band and the excited states of the acceptors. This cooling phase occurs on a time scale of tens of picoseconds (Figs. 4b and 4c). The holes having now very small excess energy, the emission rate of the optical phonons becomes very low and the acoustical phonon scattering becomes important. We, therefore, attribute the long time constant to the capture of holes in acceptor ground state by emission of acoustical phonons (Figs. 4a and 4b). We conclude that the capture of holes by ionized acceptors proceeds in two steps:

The holes relax to the excited states of the acceptors by emission of optical phonons in a fast process of order of tens of picoseconds and: Then, they relax to the ground state of the acceptors by emission of acoustical phonons on a longer time scale of hundreds of picoseconds. Our results is supported by previous Monte Carlo simulations[25] which calculate capture process of holes by ionized acceptors with two constants of time. This is in contrast with the capture process in GaAs semiconductor, which occurs by emission of a single optical phonon[26]. In GaAs, however, the ionization energy of the acceptor is of the order of 30 meV, which is about the optical phonon energy and much larger than the energy of an acoustical phonon.

In conclusion, we have presented the relaxation dynamics of holes excited into the spin-orbit split-off valence band in a p-type germanium with a temporal resolution of 250 femtoseconds. We have shown that the holes are redistributed and thermalized in the heavy-hole band within 550 femtoseconds by emission of optical phonons via the deformation potential and by inelastic hole-hole scattering. Measurements at different lattice temperatures provide us direct evidence that the capture of holes by ionized acceptors occurs in two steps. First, the holes relax to the acceptor excited states by emission of optical phonons; this process occurs on a time scale of tens of picoseconds. Subsequently, the holes are captured in the acceptor ground state by emission of acoustical phonons on a longer time scale of hundreds of picoseconds.

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